

SPECIFICATION  
POLYANILINE-CONTAINING COMPOSITION AND PRODUCTION  
METHOD THEREOF

FIELD OF THE INVENTION

The present invention relates to a polyaniline-containing composition including a polyaniline uniformly dispersed in water or a solvent, and a method for producing the same.

BACKGROUND OF THE INVENTION

Among various conductive polymers, a polyaniline, which is favorable in the stability in air, has been studied for application in various fields. Typical examples of the applications thereof include cathode for a secondary battery, a solid electrolyte capacitor, a polymer battery, a chemical sensor, a display element, an antistatic agent, an antirust agent, a transparent conductive film, an electromagnetic wave-shielding material, and the like.

In most of these applications, a polyaniline is coated on various materials for use. Properties demanded for the coated films in such a case include the productivity as well as the strength and the flexibility of the coated films, in addition to conductivity, a property inherent to the polyaniline.

However, a polyaniline is generally, extremely lower in solubility in water or a solvent and thus, gives only a film lower in polyaniline content and unsatisfactory in conductivity when used as a coating agent. Even when dispersed forcibly in water or a solvent, a polyaniline caused a problem

that it was difficult to prepare a uniformly coated film because of extremely strong cohesive force and poor dispersion state and the coated film thus obtained was insufficient in strength and flexibility.

To overcome the problem, proposed are methods of oxidative polymerization of an aniline monomer in the presence of a polymer emulsion or a water-soluble monomer and thus obtaining a polyaniline-containing composition superior in dispersion stability (e.g., JP-A Nos. 64-69621 and 4-268375, and others).

However, in these methods, the oxidative polymerization reaction of aniline in the presence of a polymer emulsion or a water-soluble monomer is very slow, giving only a polyaniline lower in molecular weight and consequently providing a coated film insufficient in conductivity. These methods also caused a problem that the composition included a large amount of unreacted aniline monomer and deteriorated the properties of the resulting coated film.

It is an object of the present invention is to provide a polyaniline-containing composition including polyaniline uniformly dispersed in water or a solvent, thus having a superior dispersion stability, and giving a coated film higher in conductivity and superior in strength and flexibility, and a method for production thereof.

## DISCLOSURE OF THE INVENTION

The method of producing an aniline-containing composition according to the present invention is characterized by dissolving or dispersing a polyaniline in a monomer mixture including a vinylpyrrolidone

as an essential component, and then polymerizing the monomer mixture.

The amount of the polyaniline blended in the monomer mixture is preferably in the range of 0.1 to 30 % by mass; and use of an emulsion polymerization as the polymerization method in working the production method is also preferable, because the principal medium in the polyaniline-containing composition obtained represents water and thus it is possible to obtain an environment-friendly polyaniline-containing composition.

It is preferable to use a surfactant having two or more aromatic rings in a molecule as an emulsifier for use in the emulsion polymerization, and the amount of the surfactant used is preferably in the range of 0.1 to 20 % by mass as solid matter with respect to the total amount of the polyaniline and the monomer mixture. Particularly preferably, the surfactant is a nonionic surfactant having a HLB in the range of 13 to 16.

In working the production method, it is effective to prepare the polyaniline-containing composition in a step (1) of dissolving or dispersing a polyaniline in a monomer mixture essentially including a vinylpyrrolidone and then polymerizing the monomer mixture, and additionally in a step of blending an inorganic compound therein. The amount of the inorganic compound blended in the step above is favorably in the range of 0.01 to 5 % by mass as solid matter with respect to 100 parts by mass of the total amount of the polyaniline and the monomer mixture.

In the present invention, it is also favorable to use a polymer having an acid group in a molecule as the emulsion polymer.

Another embodiment of the present invention is a

polyaniline-containing composition comprising a polyaniline, a dopant consisted of an emulsion polymer having an acid group in a molecule, an inorganic compound, and water; and the amount of the inorganic compound blended in the composition is preferably in the range of 0.01 to 5 parts by mass as solid matter, with respect to 100 parts by mass of the emulsion polymer.

#### BEST MODE FOR CARRYING OUT THE INVENTION

After intensive studies on the method of producing a polyaniline-containing composition wherein a polyaniline is dispersed in water or a solvent uniformly, the inventors have found that it was possible to produce a composition wherein polyaniline is uniformly dispersed easily by dissolving or dispersing a polyaniline in a monomer mixture including a vinylpyrrolidone as an essential component and then polymerizing the monomer mixture, and that it was possible to produce a coated film higher in conductivity and superior in strength and flexibility by coating the polyaniline-containing composition obtained by the method; and completed the present invention.

The polyaniline-containing composition prepared by the method of production according to the present invention is also an embodiment of the present invention.

A common emeraldine-type polyaniline is favorably used as the polyaniline mainly used as dispersed in the present invention. The emeraldine-type polyaniline is a resin including a basic skeleton having a reduced form unit (phenylenediamine skeleton) and an oxidized form unit

(quinonimine skeleton) at a molar ratio of 1:1 as a recurring unit.

However, in the present invention, which is not characterized by the polyaniline per se but by the stable uniform dispersion thereof, the polyaniline for use in the present invention may be a resin produced by any known method or a product commercially available.

In addition to the emeraldine-type polyaniline, a polyaniline having an *o*- or *m*-substituted aromatic ring in a polyaniline skeleton may be used as the polyaniline. Examples of the substituent groups which are optionally substituted with an aromatic ring in a polyaniline skeleton include, but are not limited to, an alkyl group having a carbon number of 1 to 20, an alkoxyl group having a carbon number of 1 to 20, a carboxyl ester group having a carbon number of 1 to 20, a cyano group, an aryl group, a sulfone group, a halogen group, and the like.

In the present invention, the polyaniline above may be used alone or in combination of two or more as needed at an arbitrarily ratio.

The weight-average molecular weight (Mw) of the polyaniline for use in the present invention is preferably 2,000 or more as polyethylene oxide as determined by GPC. A weight-average molecular weight of less than 2,000 may lead to deterioration in the conductivity of the coated film obtained from the polyaniline-containing composition. On the other hand, an excessively large weight-average molecular weight may lead to poor dispersion of the polyaniline, and thus, the weight-average molecular weight is favorably 300,000 or less. Considering the advantages and disadvantages above, the weight-average molecular weight of the polyaniline is more preferably in the range of 3,000 or more and 200,000 or less, and still more preferably 5,000 or

more and 100,000 or less.

During solubilization or dispersion of the polyaniline in the monomer mixture according to the present invention including a vinylpyrrolidone as an essential component, it is preferable to use an undoped polyaniline that is not doped. It is because the undoped polyaniline is higher in solubility and dispersibility in the monomer mixture including the vinylpyrrolidone.

During solubilization or dispersion of the polyaniline in the monomer mixture according to the present invention including a vinylpyrrolidone as an essential component, it is preferable to dissolve or disperse the polyaniline while the mixture is agitated strongly in a device that is capable of high-speed stirring such as a homogenizer or a homomixer.

During solubilization or dispersion of a polyaniline in the monomer mixture including a vinylpyrrolidone as an essential component, the amount of polyaniline used in the monomer mixture is preferably in the range of 0.1 % by mass or more and 30 % by mass or less. The used amount of less than 0.1 % by mass tends to lead to deterioration in the conductivity of the coated film obtained from the polyaniline-containing composition, while the used amount of more than 30 % by mass may lead to poor dispersion of the polyaniline and deterioration in the strength and the flexibility of the coated film obtained from the polyaniline-containing composition. The blended amount of the polyaniline is more preferably in the range of 0.2 % by mass or more and 20 % by mass or less, and still more preferably 0.3 % by mass or more and 10 % by mass or less.

The vinylpyrrolidones for use in the present invention are, for example, N-vinylpyrrolidone, N-vinyl-5-methyl-2-pyrrolidone, and the like.

The amount of the vinylpyrrolidone in the monomer mixture is preferably in the range of 0.1 % by mass or more and 90 % by mass or less. The used amount of less than 0.1 % by mass may lead to decrease in the solubility or the dispersibility of the polyaniline in the monomer mixture, while the used amount of more than 90 % by mass may lead to deterioration in the water resistance of the coated film obtained from the polyaniline-containing composition. The used amount is more preferably in the range of 1 % by mass or more and 50 % by mass or less and most preferably 10 % by mass or more and 30 % by mass or less.

An acid group-containing monomer is preferably added to the monomer mixture for use in the present invention as a dopant, for giving the polyaniline conductivity as it is doped. Favorable examples of the acid group-containing monomers include carboxyl group-containing monomers, sulfone group-containing monomers, phosphoric acid group-containing monomers; and specific examples thereof include (meth)acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, methacrylsulfonic acid, 3-sulfopropyl (meth)acrylate, 2-(meth)acryloyloxyethyl acid phosphate, and the like. These monomers may be used alone or in combination of two or more at an arbitrarily ratio as needed.

The amount of the acid group-containing monomer blended in the monomer mixture is preferably in the range of 0.1 % by mass or more and 40 % by mass or less. The blended amount of less than 0.1 % by mass may lead to insufficient conductivity of the coated film obtained from the polyaniline-containing composition because the polyaniline is doped less efficiently, while the blended amount of more than 40 % by mass may lead to

deterioration in the water resistance of the coated film obtained from the polyaniline-containing composition. The lower limit value of the blended amount is more preferably 0.5 % by mass, and most preferably 1.0 % by mass or more. The upper limit value of the blended amount is more preferably 30 % by mass and most preferably 20 % by mass or less.

In addition to the vinylpyrrolidone and the acid group-containing monomer, the monomer mixture may include other monomers. The kinds and amounts of other monomers used are selected properly according to the physical properties desirable for the coated film obtained from the polyaniline-containing composition.

Examples of the other monomers include (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, propyl (meth)acrylate, cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, phenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, and 1,6-hexanediol di(meth)acrylate; (meta)acrylamide, methylene bis(meta)acrylamide, styrene,  $\alpha$ -methylstyrene, vinyltoluene, divinylbenzene, and the like; and these monomers may be used alone or in combination of two or more.

The amount of the other monomers used in the total amount of the raw monomer mixture is preferably in the range of 10% by mass or more to



80 % by mass or less. It is because the used amount of less than 10 % by mass may lead to deterioration in the water resistance of the coated film, while the used amount of more than 80 % by mass may lead to decrease in the solubility and the dispersibility of polyaniline in the monomer mixture and deterioration in the conductivity of the coated film obtained. The amount of the other monomers used is more preferably 20 % by mass or more and 70 % by mass or less and still more preferably 30 % by mass or more and 60 % by mass or less.

For example, a bulk polymerization, a solution polymerization, a suspension polymerization, an emulsion polymerization, or the like may be used as the method of polymerizing the monomer mixture; and among these polymerization methods, particularly preferable is the emulsion polymerization. It is because when the emulsion polymerization is used, the principal medium in the polyaniline-containing composition obtained represents water and thus it is possible to obtain an environment-friendly polyaniline-containing composition.

Any one of common emulsion polymerization methods may be applied as the emulsion polymerization method used, and examples thereof include a simultaneous monomer addition, a dropwise monomer addition, a preemulsification, a power feeding, a seed polymerization, a multi-step monomer addition, and the like.

The conditions, for example, temperature and period, of the polymerization reaction may be selected arbitrarily, but the polymerization is preferably performed under a nitrogen atmosphere, and use of a chain transfer agent is also effective for making the adjustment of the average

molecular weight of the polymer obtained easier.

The surfactant for use when the emulsion polymerization method is employed is preferably a nonionic surfactant having a HLB (abbreviation of Hydrophile-Lipophile Balance) in the range of 13 to 16, more preferably 14 to 16, and particularly preferably 14 to 15, from the point of the stability of micelle. The HLB is an indicator indicating the balance between the hydrophilicity and the lipophilicity of a surfactant, and can be calculated by the Griffin equation:

$$\text{HLB} = (\text{mass fraction of polyoxyethylene region})/5,$$

when the surfactant is an ethylene oxide nonionic surfactant, and

$$\text{HLB} = 20[1 - (\text{saponification value of polyvalent alcohol ester})/(\text{neutralization value of fatty acid})],$$

when the surfactant is a polyvalent alcohol nonionic surfactant.

Among the nonionic surfactants, preferable are surfactants having two or more aromatic rings in the molecule skeleton, which have a high affinity with the polyaniline and keep the micelle more reliably in the emulsification state.

Examples of the aromatic rings include benzene, naphthalene, anthracene, phenanthrene, pyrrole, furan, thiophene, pyridine, benzofuran, benzothiophene, quinoline, and isoquinoline rings that may be unsubstituted or substituted, and the like; and among them, particularly preferable are benzene and naphthalene rings.

Examples of the surfactant satisfying the preferable requirements above include polyoxyethylene styrenated phenylethers, polyoxyethylene polycyclic phenylethers, and the like; and examples of the commercially

available products thereof include, but are not limited to, "Eleminol SCZ-35", "Eleminol STN-6", "Eleminol STN-8", "Eleminol STN-13", "Eleminol STN-20", and "Eleminol STN-45" (trade names, all manufactured by Sanyo Chemical Industries Ltd.); "Emulgen A-60", "Emulgen A-66", and "Emulgen A-90" (trade names, all manufactured by Kao Corporation); "Noigen EA-157", "Noigen EA-167", and "Noigen EA-177" (trade names, all manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.); and the like.

The amount of the surfactant used is preferably in the range of 0.1 to 20 % by mass as solid matter with respect to the total amount of the polyaniline and the monomer mixture. The used amount of less than 0.1 % by mass may lead to deterioration in the stability of the emulsion polymerization, while the used amount of more than 20 % by mass may lead to deterioration in the water resistance of the coated film obtained from the polyaniline-containing composition. The used amount is more preferably in the range of 1 % by mass or more and 15 % by mass or less and most preferably 5 % by mass or more and 10 % by mass or less.

In working the present invention, other surfactants may be used together with the surfactant having two or more aromatic rings in the molecule. A nonionic or anionic surfactant having one aromatic ring in a molecule is preferable as the other surfactant.

Typical examples of the nonionic surfactants include polyoxyethylene alkylpropenylphenylethers, polyoxyethylene nonylphenylethers, polyoxyethylene octylphenylethers, and the like; and examples of the anionic surfactants include sodium salts of dodecyldiphenyletherdisulfonic acid, sodium salts of naphthalenesulfonic acid/formalin condensates, and the like.

The amount of the other surfactants used is preferably in the range of 0.1 % by mass or more to 20 % by mass and less preferably 1 % by mass or more and 15 % by mass or less as solid matter, with respect to the total amount of the polyaniline and the monomer mixture.

The polymerization initiators for use in the emulsion polymerization include, for example, peroxide-base initiators such as ammonium persulfate, potassium persulfate, benzoyl peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, and cumene hydroperoxide; and particularly preferable are azo-based polymerization initiators, which are less oxidative to polyaniline. Typical examples of the azo-based polymerization initiators include water-soluble azo compounds such as azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2-amidinopropane) dihydrochloride, and 4,4'-azobis(4-cyanopentanoic acid), and the like.

The amount of the polymerization initiator used is preferably in the range of 0.1 parts or more and 5 parts or less by mass with respect to 100 parts by mass of the monomer mixture. The used amount of less than 0.1 parts by mass may result in slower progress of the emulsion polymerization, leaving more unreacted monomers, and deterioration in the strength and the flexibility of the coated film obtained from the polyaniline-containing composition, while the used amount of the polymerization initiator of more than 5 parts by mass, which is excessively high, may result in deterioration in the stability of the emulsion polymerization. The used amount is more preferably in the range of 0.5 parts or more and 3 parts or less by mass, and most preferably 0.7 parts or more and 2 parts or less by mass.

The content of the polyaniline in the polyaniline-containing

composition obtained by the present invention is preferably in the range of 0.01 % by mass or more and 10 % by mass or less. The content of less than 0.01 % by mass may lead to deterioration in the conductivity of the coated film obtained from the polyaniline-containing composition, while an excessively high concentration of more than 10 % by mass may lead to poor dispersion of the polyaniline and deterioration in the strength and the flexibility of the coated film obtained from the polyaniline-containing composition. The content of polyaniline is more preferably 0.1 % by mass or more and 5 % by mass or less and still more preferably 0.3 % by mass or more and 3 % by mass or less.

The total amount of the polyaniline and the emulsion polymer in the polyaniline-containing composition according to the present invention is preferably in the range of 5 % by mass or more and 60 % by mass or less in the composition. The total amount of less than 5 % by mass may lead to deterioration in the efficiency of forming a coated film obtained from the polyaniline-containing composition, while an amount of more than 60 % by mass may lead to deterioration in the stability of the polyaniline-containing composition. The total amount is more preferable in the range of 7 % by mass or more and 40 % by mass or less, and most preferably in the range of 10 % by mass or more and 30 % by mass or less.

Among the emulsion polymers obtained by the emulsion polymerization of the monomer mixture in the polyaniline-containing composition obtained by the present invention, a polymer having an acid group in a molecule is preferable, as it acts on the polyaniline as a dopant, facilitating uniform dispersion of the polyaniline and raising the conductivity

of the coated film obtained from the composition further.

Namely, the doped polyaniline is in the state of its polyaniline protonated and the dopant is a compound supplying the proton, and thus, the polymer having an acid group in a molecule is effective in that action. Thus, a selective use of a monomer having an acid group in a molecule in the monomer mixture which is a source for producing the emulsion polymer is extremely preferable for increasing the function of the emulsion polymer as a dopant.

The emulsion polymer preferably has a weight-average molecular weight ( $M_w$ ) in the range of 2,000 to 500,000. A weight-average molecular weight of less than 2,000 may lead to deterioration of the strength and the water resistance of the coated film obtained from the polyaniline-containing composition, while that of more than 500,000 tends to decrease in the solubility and the dispersibility of the emulsion polymer in water. The weight-average molecular weight ( $M_w$ ) of the emulsion polymer is more preferably in the range of 5,000 to 200,000 and most preferably 10,000 to 100,000.

To maximize the function of the emulsion polymer as a dopant, it is preferable to adjust the content of the emulsion polymer in the polyaniline-containing composition into the range of 10 % by mass or more and 60 % by mass or less as solid matter. The content of less than 10 % by mass may lead to decrease in the efficiency of forming a coated film obtained from the polyaniline-containing composition, and thus a uniformly coated film can not be produced, while the content of more than 60 % by mass may lead to increase in the viscosity of the polyaniline-containing composition,

resulting in deterioration of the efficiency of forming the coating film. The content is more preferably in the range of 15 % by mass or more and 50 % by mass or less, and most preferably 20 % by mass or more and 40 % by mass or less.

It is also effective to add an inorganic compound in a suitable amount, in addition to the polyaniline and the emulsion polymer acting as a dopant, to the polyaniline-containing composition according to the present invention. It is because presence of an inorganic compound suppresses the self-aggregating tendency of the polyaniline and increases the storage stability (separation stability) of the composition further.

In this manner in the polyaniline-containing composition according to the present invention comprising a polyaniline, an emulsion polymer acting as a dopant and having an acid group in a molecule, an inorganic compound, and water, the polyaniline raises the conductivity of the coated film, the polyaniline keeps its uniform dispersion state as it is doped with the emulsion polymer having an acid group in the molecule, and the inorganic compound raises the storage stability further by reducing aggregation of the polyaniline adhered to the emulsion polymer; thus, it becomes possible to obtain a composition giving a coated film higher in conductivity and superior in strength and flexibility by using it as a coating agent, in the synergic effect of these actions.

The inorganic compound for use in the composition is preferably inorganic particles such as inorganic fine particles having a specific surface area of 50 m<sup>2</sup>/g or more. Inorganic particles having a specific surface area of less than 50 m<sup>2</sup>/g are not effective in suppressing aggregation of a

polyaniline, and may lead to decrease in the effectiveness of the improvement in storage stability by addition of the inorganic fine particles. The specific surface area of the inorganic particles is more preferably 100 m<sup>2</sup>/g or more, and most preferably 150 m<sup>2</sup>/g or more.

The average particle diameter of the primary particles of the inorganic particle is preferably 50 nm or less. The average particle diameter of the primary particles of inorganic particle at more than 50 nm may lead to aggregation of a polyaniline over time and decrease in the storage stability of the composition. The average particle diameter of the primary particles of the inorganic particle is preferably 30 nm or less, and most preferably 20 nm or less.

Examples of the inorganic compounds include silica, alumina, zirconia, titania, silicon carbide, silicon nitride, boron carbide, boron nitride, carbon, and the like. Among these inorganic compounds, preferable are inorganic oxides such as silica, alumina, zirconia, and titania, which improve the stability of the polyaniline-containing composition; and particularly preferable is silica particles.

Examples of the silica particles include fumed silica, colloidal silica, and the like, and typical examples thereof include "Aerosil " (trade name, manufactured by Nippon Aerosil Co., Ltd.), "Rheoloseal" (trade name, manufactured by Tokuyama Corp.), and the like.

The amount of the inorganic compound blended is preferably in the range of 0.01 to 5 parts by mass with respect to 100 parts by mass of the solid matters in emulsion polymer. The blended amount of less than 0.01 parts by mass may result in decrease in the effectiveness of suppressing



aggregation of a polyaniline and almost ineffectiveness in improving storage stability, while the blended amount of more than 5 parts by mass may result in decrease in the strength and the flexibility of the coated film obtained from the polyaniline-containing composition. The blended amount of the inorganic compound is more preferably 0.1 parts or more and 3 parts or less by mass, still more preferably 1 part or less by mass.

Any common method may be used for blending the inorganic compound, but most preferable is a method of blending the inorganic compound in the polyaniline doped and stabilized with the emulsion polymer having an acid group in a molecule.

The polyaniline-containing composition obtained by the present invention may include other compounds and secondary materials as needed. Examples of the other compounds and secondary materials include an antioxidant, an ultraviolet absorbent, an ultraviolet stabilizer, a plasticizer, a leveling agent, a repulsion inhibitor, a solvent, and the like.

The amount of the other compounds and the secondary materials blended is not particularly limited if it is in the range that does not impair the advantageous effects of the present invention, but preferably in the range of 0.001 parts or more and 10 parts or less by mass with respect to 100 parts by mass of the composition.

When used as a coating agent, the polyaniline-containing composition according to the present invention may be coated on a particular base material by any method, for example, brush coating, roll coating, spray coating, dip coating, or the like. After coating, a coated film may be formed by drying at normal temperature or heat-drying at a temperature of

approximately 50 to 150°C, and in this manner, it is possible to produce a uniformly coated film higher in conductivity and superior in strength and flexibility. Accordingly, the composition can be used favorably as a raw material for antistatic agent, capacitor, battery, EMI shield, chemical sensor, display element, and the like.

## EXAMPLES

Hereinafter, the present invention will be described in more detail with reference to Examples, but it should be understood that the present invention is not restricted by the following Examples and can be properly modified within the scope described above or below and such modifications are also included in the technical scope of the present invention. In Examples below, "%" means "% by mass ", and "part" means "part by mass" respectively, unless specified otherwise.

Evaluation test methods used in the following Examples are as follows:

[Evaluation test methods]

### (a) Surface resistance

A coated film having a thickness of 2  $\mu\text{m}$  was formed by coating a sample polyaniline-containing composition on a glass plate to a thickness of about 2  $\mu\text{m}$  with a bar coater and drying the coated film at 120°C for 30 minutes, and the surface resistance of each coated film was determined according to JIS K6911.

### (b) Appearance

A coated film having a thickness of 2  $\mu\text{m}$  was formed on a

chromate-finished aluminum substrate by coating a sample polyaniline-containing composition with a bar coater and drying the coated film at 120°C for 30 minutes, and the appearance thereof was evaluated by visual observation.

○... Uniform coated film formed

△... Partial aggregation observable

×... Many aggregates observable

(c) Pencil hardness measurement

A coated film having a thickness of 2  $\mu\text{m}$  was formed by coating a sample polyaniline-containing composition on a chromate-finished aluminum substrate with a bar coater to a thickness of about 2  $\mu\text{m}$  and drying the coated film at 120°C for 30 minutes, and the pencil hardness of the coated film was determined according to JIS K6911.

(d) Dispersion stability

Each sample polyaniline-containing composition was left in a thermostatic oven at 30°C and the dispersion state of the sample was evaluated once a month.

○... Homogeneous dispersion,

△... Tendency to partial separation

×... Tendency to drastic separation

Example 1

Ten parts of polyaniline (emeraldine-based polyaniline, trade name: "PANIPOL PA", manufactured by Panipol) as a polyaniline was dissolved uniformly in 20 parts of N-vinylpyrrolidone, to give a blue purple polyaniline

solution. The solution was added dropwise into a liquid mixture of 20 parts of styrene, 5 parts of butyl acrylate, and 5 parts of acrylic acid while the mixture was stirred in a homogenizer, to give a dark green monomer mixture in which polyaniline was dispersed uniformly.

140 parts of ion-exchange water and 1.8 parts of a surfactant (trade name: "Nonipol 200", manufactured by Sanyo Chemical Industries Ltd.) were placed in a reactor equipped with a thermometer, a condenser tube, a nitrogen-supply tube, a dropping funnel, and a stirrer, and the mixture was dissolved while agitated under nitrogen gas flow. The monomer mixture was placed in the dropping funnel and one tenth of it was added dropwise into the reactor, and then, 12 parts of a 5% aqueous 2,2'-azobis(2-amidinopropane)dihydrochloride salt solution was added thereto.

After polymerization reaction at 70°C for 30 minutes, the remaining monomer mixture was added dropwise over 2 hours. After dropwise addition, the polymerization reaction was continued at the same temperature additionally for 1 hour, to give a polyaniline-containing composition (1) according to the invention including nonvolatile matters and polyaniline respectively at concentrations of 29% and 4.5%.

## Example 2

Five parts of polyaniline was dissolved in 20 parts of N-vinylpyrrolidone uniformly, to give a blue purple polyaniline solution. The solution was added dropwise into a liquid mixture of 20 parts of styrene, 15 parts of butyl acrylate, and 5 parts of

2-acrylamido-2-methyl-1-propanesulfonic acid while the mixture was stirred in a homogenizer, to give a dark green monomer mixture in which polyaniline was dispersed uniformly.

Then, the mixture was allowed to react in emulsion polymerization reaction in a similar manner to Example 1, to give a polyaniline-containing composition (2) according to the invention containing nonvolatile matters and polyaniline respectively at concentrations of 31% and 2.2%.

### Example 3

Three parts of polyaniline was dissolved in 20 parts of N-vinylpyrrolidone uniformly, to give a blue purple polyaniline solution. The solution was added dropwise into a liquid mixture of 20 parts of styrene, 10 parts of butyl acrylate, and 3 parts of 2-methacryloyloxyethyl acid phosphate while the mixture was stirred in a homogenizer, to give a dark green monomer mixture in which polyaniline was dispersed uniformly.

Then, the mixture was allowed to react in emulsion polymerization reaction in a similar manner to Example 1, to give a polyaniline-containing composition (3) according to the invention containing nonvolatile matters and polyaniline respectively at concentrations of 28% and 1.4%.

### Reference Example 1

A liquid mixture of 20 parts of N-vinylpyrrolidone, 20 parts of styrene, 5 parts of butyl acrylate, and 5 parts of acrylic acid were placed in a dropping funnel, and emulsion polymerization reaction was performed in a similar manner to Example 1, to give an emulsion composition (1) containing

nonvolatile matters at a concentration of 22%.

#### Comparative Example 1

Ten parts of 12N hydrochloric acid and 4.65 parts of aniline were dissolved in 150 parts of the emulsion composition (1) obtained in Reference Example 1. Separately, an aqueous oxidizer solution of 11.4 parts of ammonium persulfate dissolved in 100 parts of ion-exchange water was prepared. After cooled to 5°C, these two solutions were mixed and allowed to react for 8 hours while agitated, to give a comparative polyaniline-containing composition (comparative composition 1) including nonvolatile matters and polyaniline respectively at concentrations of 13% and 1.3%. The reaction rate of the oxidative polymerization of aniline in the reaction was 80%.

#### Comparative Example 2

Five parts of dodecylbenzenesulfonic acid and 5 parts of polyaniline (trade name: "PANIPOL PA", manufactured by Panipol) were mixed in 150 parts of the emulsion composition (1) obtained in Reference Example 1 above while the mixture was agitated in a homogenizer, to give a comparative polyaniline-containing composition (comparative composition 2) including nonvolatile matters and polyaniline respectively at concentrations of 27% and 3.1%.

Properties of the respective polyaniline-containing compositions obtained Examples and Comparative Examples above were evaluated by the methods described above, and the results are summarized in

Table 1.

Table 1

	Polyaniline-containing composition	Surface resistance ( $\Omega/\text{cm}^2$ )	Appearance	Pencil hardness
Example 1	(1)	$1.0 \times 10^6$	○	H
Example 2	(2)	$2.5 \times 10^6$	○	H
Example 3	(3)	$4.0 \times 10^6$	○	H
Comparative Example 1	(Comparative composition 1)	$6.5 \times 10^6$	△	B
Comparative Example 2	(Comparative composition 2)	$1.0 \times 10^6$	×	2B

As apparent from Table 1, the polyaniline-containing compositions obtained in Examples 1 to 3, in which polyaniline was dispersed uniformly, gave a uniform coated film higher in conductivity and sufficient in the strength and flexibility of coated film.

In contrast, the comparative polyaniline-containing composition of Comparative Example 1, in which polyaniline was dispersed partially unevenly and the polymerization degree of aniline was lower, gave a coated film lower in conductivity and insufficient in the strength and flexibility of coated film under the influence of the residual aniline monomer. In addition, the coated film obtained in Comparative Example 2 had almost no conductivity because of poor dispersion of polyaniline and was also insufficient in the strength and flexibility of coated film.

#### Example 4

Two parts of polyaniline was uniformly dissolved in a mixture of 20 parts of N-vinylpyrrolidone and 2 parts of water, to give a blue purple polyaniline solution. The solution was added dropwise into a liquid mixture of 20 parts of styrene, 5 parts of butyl acrylate, and 2 parts of 2-acrylamido-2-methyl-1-propanesulfonic acid while agitated in a homogenizer, to give a dark green monomer mixture in which polyaniline was dispersed uniformly.

140 parts of ion-exchange water and 3 parts of a surfactant having two or more aromatic rings in the molecule (polyoxyethylene polycyclic phenylether, trade name: "Eleminol SCZ-35", manufactured by Sanyo Chemical Industries Ltd., HLB: 14.6) were placed in the reactor equipped with a thermometer, a condenser tube, a nitrogen-supply tube, a dropping funnel, and a stirrer, and dissolved while agitated under nitrogen gas flow. The monomer mixture was placed in the dropping funnel and one tenth of it was added dropwise into the reactor, and then, 5 parts of a 20% aqueous 2,2'-azobis(2-amidinopropane) dihydrochloride salt solution was added thereto. After polymerization at 70°C for 30 minutes, the remaining monomer mixture was added dropwise over 4 hours. After dropwise addition, the polymerization reaction was continued at the same temperature additionally for 2 hours, to give a polyaniline-containing composition (4) including a sulfonic acid group-containing emulsion polymer as a dopant. The composition (4) included nonvolatile matters and polyaniline respectively at concentration of 29% and 1.0%.

#### Example 5



A polyaniline-containing composition (5) according to the invention was prepared in a similar manner to Example 4 above, except that a surfactant having two aromatic rings in the molecule (polyoxyethylene styrenated phenylether, trade name: "Noigen 157", manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd., HLB: 14.3) was used. The composition (5) included nonvolatile matters and polyaniline respectively at concentration of 29% and 1.0%.

#### Example 6

Two parts of polyaniline was dissolved in a mixture of 20 parts of N-vinylpyrrolidone and 2 parts of water uniformly, to give a blue purple polyaniline solution. The solution was added dropwise into a liquid mixture of 20 parts of styrene, 10 parts of butyl acrylate, 2 parts of 2-acrylamido-2-methyl-1-propanesulfonic acid, and 2 parts of a surfactant (trade name: "Aqualon RN-20", manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) while the mixture was agitated in a homogenizer, to give a dark green monomer mixture in which polyaniline was dispersed uniformly.

140 Parts of ion-exchange water and 3 parts of a surfactant (trade name: "Noigen EA-167", manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) were placed in a reactor equipped with a thermometer, a condenser tube, a nitrogen-supply tube, a dropping funnel and a stirrer, and stirred and dissolved under nitrogen gas flow. The monomer mixture was placed in the dropping funnel and one tenth of it was added dropwise into the reactor, and 5 parts of a 20% aqueous 2,2'-azobis(2-amidinopropane) dihydrochloride salt solution was added thereto. After polymerization at 70°C for 30 minutes,

the remaining monomer mixture was added dropwise over 4 hours. After dropwise addition, the polymerization reaction was continued at the same temperature additionally for 2 hours, to give a polyaniline-containing composition (6) according to the invention. The composition (6) included nonvolatile matters and polyaniline respectively at concentration of 27% and 1.0%.

A coated film was formed by using each of the compositions (4) to (6) obtained in Examples 4 to 6, and the properties thereof were determined according to the evaluation methods above; as shown in the following Table 2, each coated film was superior in conductivity and also in appearance and film properties.

Table 2

	Polyaniline-containing composition	Surface resistance ( $\Omega/\text{cm}^2$ )	Appearance	Pencil hardness
Example 4	(4)	$1.0 \times 10^6$	○	HB
Example 5	(5)	$1.1 \times 10^6$	○	H
Example 6	(6)	$1.0 \times 10^6$	○	H

#### Examples 7 to 11

0.25 Parts of silica particle (trade name "Aerosil 200", manufactured by Nippon Aerosil Co., Ltd.) was added and dispersed uniformly as the inorganic compound in 100 parts (emulsion polymer content: 28 parts) of each of the polyaniline-containing compositions (1), (2) and (4) to (6) obtained Examples 1, 2 and 4 to 6, to give each of polyaniline-containing compositions

(7) to (11) in which silica powder is dispersed uniformly.

Evaluation of the dispersion stability (storage stability) of the compositions obtained (7) to (11) by the method above showed that there was no precipitate formed in any of the compositions even after two months and confirmed that the compositions were superior in dispersion stability. The properties of the coated film obtained by coating each composition were determined according to the evaluation methods above; and as shown in Table 3, the compositions were superior both in conductivity and film properties.

Table 3

	Polyaniline-containing composition	Surface resistance ( $\Omega/\text{cm}^2$ )	Appearance	Pencil hardness
Example 7	(7)	$1.0 \times 10^6$	○	HB
Example 8	(8)	$1.1 \times 10^6$	○	HB
Example 9	(9)	$1.0 \times 10^6$	○	HB
Example 10	(10)	$1.1 \times 10^6$	○	H
Example 11	(11)	$1.1 \times 10^6$	○	H

## INDUSTRIAL APPLICABILITY

The present invention, which is characterized as described above, provides a stable dispersion wherein polyaniline is dispersed uniformly, and gives a coated film higher in conductivity and superior in strength and flexibility when the composition is coated. Thus, because of the superior properties, the polyaniline-containing composition obtained by the present

invention can be used effectively and widely in applications where conductivity is desirable including applications such as an antistatic agent, an capacitor, battery, an EMI shield, an chemical sensor, and an display element.